

CPP 18: Molecular Electronics and Photonics

Time: Tuesday 9:30–12:45

Location: H42

CPP 18.1 Tue 9:30 H42

Coupled Electron-Nuclear Dynamics in Non-Adiabatic Processes — ●FEDERICA AGOSTINI¹, ALI ABEDI², FLORIAN G. EICH³, NEEPA T. MAITRA⁴, SEUNG KYU MIN⁵, ARNE SCHERRER⁶, AXEL SCHILD¹, DANIEL SEBASTIANI⁶, YASUMITSU SUZUKI⁷, RODOLPHE VUILLEUMIER⁸, and E. K. U. GROSS¹ — ¹MPI of Microstructure Physics, Halle, Germany — ²Universidad del País Vasco, San Sebastián, Spain — ³MPI for the Structure und Dynamics of Matter, Hamburg, Germany — ⁴CUNY, New York, USA — ⁵UNIST, Ulsan, South Korea — ⁶MLU Halle-Wittenberg, Halle, Germany — ⁷University of Science, Tokyo, Japan — ⁸UPMC, Paris, France

The Born-Oppenheimer (BO) approximation is widely employed to describe dynamical processes in molecular systems, based on the assumption that the typical time-scales of electronic and nuclear motion are adiabatically separable. This hypothesis allows to write the electron-nuclear wave function as a single product of an electronic eigenstate and a time-dependent nuclear wave function. Such an approximation, however, is not suited when non-adiabatic effects due the coupling between the nuclear motion and excited electronic states are important. The talk will show how the BO approximation can be made exact [PRL 105 (2010)], by preserving the single product form of the full wave function. This exact factorization approach will be introduced and used as a tool [PRL 110 (2013); JCP 142 (2015)] to interpret non-adiabatic processes. Algorithms will be derived [JCP 141 (2014); PRL 115 (2015); JCP 143 (2015)] to describe electronic non-adiabatic processes solving nuclear dynamics in terms of classical trajectories.

CPP 18.2 Tue 9:45 H42

Bending a chromophore in well-defined π -conjugated polygonic model systems: impact on photophysical properties — ●PHILIPP WILHELM¹, THOMAS STANGL¹, NINA SCHÖNFELDER², GEORGIY POLUEKTOV², SIGURD HÖGER², JAN VOGELSANG¹, and JOHN M. LUPTON¹ — ¹Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany — ²Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany

Conjugated polymers are a prime example for the complex interplay between morphology and function. Single-molecule spectroscopy has helped us in unraveling the large heterogeneity in this class of materials. But it has become apparent that even a single conjugated polymer chain contains such a complexity that it is difficult to derive a microscopic picture of the photophysical processes taking place in a single chain. We therefore introduce π -conjugated polygonic model systems, which all consist of a certain number of the same chromophoric unit. If we reduce this number the degree of bending increases, which makes the investigated molecules ideal candidates to study the impact of chromophore bending on spectroscopic observables. We go from the ensemble to the single molecule level to unmask the heterogeneity within the systems. By comparing the spectroscopic properties of molecules between different groups as well as the heterogeneity within a group, we can extract the influence of bending on the spectral properties. Extrapolating the results obtained from these systems onto conjugated polymers provides a highly heterogeneous picture regarding single chromophores that can exist on a conjugated polymer chain.

CPP 18.3 Tue 10:00 H42

Controlling position and orientation of molecules in a thin plastic film — ●FELIX HOFMANN¹, DOMINIK WÜRSCH¹, VIKAS AGGARWAL², STEFAN-S. JESTER², JAN VOGELSANG¹, SIGURD HÖGER², and JOHN LUPTON¹ — ¹University of Regensburg, Regensburg, Germany — ²University of Bonn, Bonn, Germany

For many single-molecule applications it is mandatory to embed the molecules under investigation in non-fluorescent host matrices. Single molecule spectroscopy was used to determine the position and orientation of molecules utilizing a monodisperse ring-shaped model system with a high triplet yield. The triplet state can be easily depopulated under ambient conditions for molecules close to the surface, but remains partly unquenched inside the film. Therefore, the fluorescence intensity serves as an observable for the spatial distribution of the molecules inside the film. The ring-shaped structure of the molecule together with excitation polarization spectroscopy reveals the orientation of the molecule with respect to the sample plane. A low modulation in intensity upon rotation of the polarisation of the laser indicates

a molecule oriented flat with respect to the sample plane whereas a high modulation means that it is oriented perpendicularly to the sample plane. As an additional step in sample preparation, solvent vapor annealing enables diffusion of the molecules within the host matrix. This is achieved by applying a constant flow of solvent-saturated nitrogen to the sample, which lowers the glass transition temperature of the film. We found that after this additional treatment, all molecules lie flat with respect to the surface close to the plastic/air interface.

CPP 18.4 Tue 10:15 H42

Photon-correlation studies on single para-xylylene bridged perylene bisimide macrocycles — ●ULRICH MÜLLER¹, PETER SPENST², MATTHIAS STOLTE², FRANK WÜRTHNER², and JENS PFLAUM^{1,3} — ¹Experimentelle Physik VI, Julius-Maximilians-Universität, Würzburg — ²Institut für Organische Chemie, Julius-Maximilians-Universität, Würzburg — ³ZAE Bayern, Würzburg

Future communication technologies demand for non-classical light sources based on efficient quantum emitters like organic molecules. The chemical variability and tunable fluorescence by proper substituents render Perylene Bisimides (PBIs) interesting candidates for implementation in single photon devices.

We will highlight the excitation dynamics of para-xylylene bridged PBI-macrocycles by means of photon-correlation measurements. These compounds show remarkable optical properties due to fast excitation energy transfer between the PBI entities [1]. We compare macrocycles with three and four chromophores with the PBI reference and show that the absorption cross section can be enhanced and the interaction with the surrounding matrix can be reduced while all macrocycles under study behave as single photon emitters. Utilizing the distribution of inter-photon delay times $g^{(2)}$ we determine the radiative transition rate $0.16(2)\text{ns}^{-1}$ from the excited S1 to the ground state.

Our study advances the understanding of excitation and relaxation processes in multichromophoric systems and thus, promotes their application as single photon emitters.

[1] F. Schlosser et al., *Chem. Sci.* **3**, 2778 (2012)

CPP 18.5 Tue 10:30 H42

Ultrahigh time-resolution two-dimensional spectroscopy of polymer thin films — ANTONIETTA DE SIO^{1,2}, ●EPHRAIM SOMMER^{1,2}, FILIPPO TROIANI³, JULIEN RÉHAULT⁴, MARGHERITA MAIURI⁴, GIULIO CERULLO⁴, ELISA MOLINARI³, and CHRISTOPH LIENAU^{1,2} — ¹Institut für Physik, Carl von Ossietzky Universität, 26197 Oldenburg, Germany — ²Center of Interface Science, Carl von Ossietzky Universität, 26129 Oldenburg, Germany — ³Instituto Nanoscienze - CNR, Centro S3, via Campi 213a, 41125 Modena, Italy — ⁴IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, 20133 Milano, Italy

Organic semiconductors have the remarkable property that their optical excitation not only generates charge-neutral electron-hole pairs (excitons) but also charge-separated polaron pairs with high yield. Although it is known that polaron pairs are formed on an ultrafast time scale, the microscopic mechanisms governing this formation are debated. We use two-dimensional optical spectroscopy to study this formation in a prototypical polythiophene thin film with 10-fs time resolution. These spectra revealed multi-period oscillations with ~ 20 fs period, persisting for hundreds of femtoseconds, and peak splittings as signatures of persistent vibronic coherence at room temperature. Our data suggest that strong vibronic coupling causes polaron pair formation on a sub-20-fs time scale, accelerates charge separation dynamics and makes it insensitive against disorder-induced fluctuations of the vibronic levels.

CPP 18.6 Tue 10:45 H42

Electronic Properties of Optically Switchable Photochromic Diarylethene Molecules at Interface with Organic Semiconductors — ●QIANKUN WANG¹, JOHANNES FISCH¹, BJÖRN KOBIN², STEFAN HECHT², and NORBERT KOCH¹ — ¹Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 6, 12489 Berlin, Germany — ²Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

Photochromic organic molecules have attracted increasing interest for the development of low-cost multifunctional devices. Diarylethene

(DAE) molecules, which are among the most interesting photochromes, show promising application potentials due to their high fatigue resistance and thermal bistability, and the interface energetics of DAE-based (bulk and planar) heterojunction is of high importance for understanding the effects on charge transport in photoswitchable devices. Here, the valence electronic structure upon switching of a photochromic diarylethene derivative, 1,2-bis(2-methyl-5-p-tolylthiophen-3-yl) cyclopent-1-ene (DAE1) was measured by ultraviolet photoelectron spectroscopy. Switching between open and closed forms was followed in situ upon appropriate illumination with ultraviolet and visible light, respectively. The energy level alignment at interfaces between DAE1 and organic hole (electron) transport materials was observed to be affected by the photoisomerization process, which resulted in different charge transport energy barriers for holes (electrons) before and after light irradiation. Our experimental findings provide a rationale for photo-control of charge transport in organic electronic devices.

15 min. break

CPP 18.7 Tue 11:15 H42

Organic heterojunctions: Contact-induced molecular re-orientation, interface states, and charge re-distribution — ●ANDREAS OPITZ¹, ANDREAS WILKE¹, PATRICK AMSALEM¹, ULRICH HÖRMANN², ELLEN MOONS³, and NORBERT KOCH^{1,4} — ¹Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany — ²Institute of Physics, University of Augsburg, Augsburg, Germany — ³Department of Engineering and Physics, Karlstad University, Karlstad, Sweden — ⁴Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

The planar heterojunction formed between the hydrogen and fluorine terminated copper phthalocyanines has been found to behave as charge generation layer [1]. Therefore, this interface was investigated by ultraviolet photoelectron and X-ray absorption spectroscopy. Pinning at the Fermi level of the underlying electrode is observed for both materials—one p type and the other one n type. This results in a sheet charge density at the organic/organic interface due to interfacial charge transfer. An interlayer with co-facial intermolecular arrangement, which differs from the respective bulk structures, at the interface was found by both spectroscopy techniques; this interlayer, noteworthy, is unpinned.

[1] A. Opitz et al., *Org. Electron.* **10** (2009) 1259–1267.

CPP 18.8 Tue 11:30 H42

Activation of Organometallic Dimers as n-Dopants for a Low Electron Affinity Organic Semiconductor — ●BERTHOLD WEGNER¹, XIN LIN², KARTTIKAY MOUDGIL³, STEPHEN BARLOW³, SETH R. MARDER³, ANTOINE KAHN², and NORBERT KOCH¹ — ¹Humboldt-Universität zu Berlin, Germany — ²Princeton University, USA — ³Georgia Institute of Technology, USA

In the past years, several methods were developed to n-dope organic semiconducting materials in order to increase their conductivities. So far, however, these methods were only able to n-dope organic materials with electron affinities (EAs) as low as 4.0 eV. Recently, Guo et al. [1] introduced a new approach using organometallic dimers as air-stable precursors, with which they were able to n-dope several organic materials with EAs ranging down to 2.8 eV. In this work, we investigated the use of ultraviolet (UV) light to activate the n-doping of the low EA (2.4 eV) electron transport material phenyl-dipyrenylphosphine oxide (POPy₂) with two different organometallic dimers. Changes in the work function and conductivity of doped POPy₂ samples are measured for various doping concentrations using non-invasive contact potential difference and current-voltage measurements in the dark and in ultrahigh vacuum. Within only a few seconds of UV illumination, the conductivity was found to increase over several orders of magnitude and the Fermi level to be pinned at 2.6 eV. While both dimers show the same trends in their general doping behavior, they also differ in some details for which possible reasons are discussed.

[1] Guo et al. *Adv. Mater.* **24**, 699-703 (2012).

CPP 18.9 Tue 11:45 H42

Conduction mechanisms in polypyrrole (PPy)/pc-ZnO heterojunctions: role of the amount of FeCl₃ as oxidizing agent — ●ALEJANDRA CASTRO-CARRANZA¹, JAIRO C. NOLASCO², STEPHANIE BLEY¹, FLORIAN MEIERHOFER³, LUTZ MÄDLER³, TOBIAS VOSS⁴, and JÜRGEN GUTOWSKI¹ — ¹Institute of Solid State Physics, Semiconductor Optics, University of Bremen, 28359 Bremen — ²Energy and Semiconductor Research Laboratory, Carl von Ossiet-

zky University of Oldenburg, 26129 Oldenburg. — ³Foundation Institute of Material Science (IWT), Department of Production Engineering, University of Bremen, 28359 Bremen. — ⁴Institute of Semiconductor Technology, TU Braunschweig University of Technology, 38092 Braunschweig.

The current-voltage characteristics of p-n hybrid heterojunctions based on polypyrrole (PPy) and polycrystalline ZnO (pc-ZnO) are analyzed by means of an electrical equivalent circuit. PPy is grown by oxidative chemical vapor deposition under three different amounts of FeCl₃ used as oxidizing agent. The extracted parameters, together with the observed morphology of the PPy and the turn-on voltage values of the respective devices indicate that thermionic emission of holes occurs at the PPy/pc-ZnO heterojunction. For larger FeCl₃ amounts used, an increment of recombination by tunneling of carriers occurs attributed to a narrowing of the depletion region due to an increment of traps states. These physical mechanisms are discussed on a schematic band diagram.

CPP 18.10 Tue 12:00 H42

The effect of intermolecular interaction on excited states in p-DTS(FBTTH₂)₂ — ●MARKUS REICHENBERGER^{1,2}, JOHN A. LOVE³, ALEXANDER RUDNICK^{1,2}, SERGEY BAGNICH¹, FABIAN PANZER^{1,2}, ANNA STRADOMSKA⁴, GUILLERMO C. BAZAN³, THUC-QUYEN NGUYEN³, and ANNA KÖHLER^{1,2} — ¹Experimental Physics II — ²Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth, 95440 Bayreuth, Germany — ³Center for Polymers and Organic Solids, Departments of Chemistry & Biochemistry and Materials, University of California, Santa Barbara, California 93106, United States — ⁴School of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom

Using optical spectroscopy in solution and thin film, and supported by quantum chemical calculations, we investigated the aggregation process of the donor-acceptor type molecule p-DTS(FBTTH₂)₂. We demonstrate that cooling a solution induces a disorder-order phase transition that proceeds in three stages analogous to the steps observed in semi-rigid conjugated polymers. By analyzing the spectra we are able to identify the spectral signature of monomer and aggregate in absorption and emission. From this we find that in films the fraction of aggregates is near 100 % which is in contrast to films made from semi-rigid conjugated polymers.

CPP 18.11 Tue 12:15 H42

Optical and structural properties of electrochemically prepared porphyrin thin films — ●KRISTINA LOVREK^{1,2}, KARSTEN HINRICH², KLAUS RADEMANN³, FELIX RÖSICKE^{1,4}, and JÖRG RAPPICH⁴ — ¹Humboldt-Universität zu Berlin, School of Analytical Chemistry Adlershof (SALSA), Unter den Linden 6, 10099 Berlin — ²Leibnitz-Institut für Analytische Wissenschaften - ISAS - e.V., ISAS Berlin, Schwartzschildstrasse 8, 12489 Berlin — ³Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Strasse 2, 12489 Berlin — ⁴Helmholtz-Zentrum Berlin für Materialien und Energie GmbH Inst. Silizium-Photovoltaik, Kekuléstrasse. 5, D-12489 Berlin

Properties of thin porphyrin films on semiconductor surface for use in electronic devices are investigated. Thin porphyrin films were prepared via three different synthetic routes. Different optical techniques are used for investigation of their optical and structural properties. Atomic force microscopy, UV/vis and infrared in-situ ellipsometry are used to obtain information on their optical constants, layer thickness, interactions between molecules, mechanism of reaction and structural changes. Spectral information is obtained with IR reflection spectroscopy and IR ellipsometry. Vibrational bands are analyzed with respect to the chemistry and structure.

CPP 18.12 Tue 12:30 H42

Direct probe of injection efficiency in asymmetric coplanar organic transistors — ●KARIN ZOJER¹, THOMAS ROTHLÄNDER², HERBERT GOLD², ANJA HAASE², and BARBARA STADLOBER² — ¹Institute of Solid State Physics and NAWI Graz, Graz University of Technology, Graz, Austria — ²MATERIALS Institute for Surface Technologies and Photonics, JOANNEUM RESEARCH Forschungsgesellschaft mbH, 8160 Weiz, Austria

Injection of carriers from the metal contacts into organic semiconductors crucially determines the performance of organic electronic devices, as mobile charges must essentially be provided by the contact. Asymmetric coplanar transistors with overlaps or single-sided small gaps be-

tween source/drain and gate electrode allow us to locally modify the electric field solely near the injecting contact. Utilizing self-aligned nanoimprint lithography interlayer electrode offsets between -0.2 - $1.7 \mu\text{m}$ were realized. Given that injection typically occurs via Schottky-type barriers, the comparison of the operation of the same device with

either source-sided gap or drain-sided gap directly probes the impact of the electric field on the injection efficiency without changing biases and injection barriers. We explain that transistors with a gap between source and gate electrode operate and that the profound reduction in current can be attributed to inhibited injection.